

INVESTIGATION Of NanoPt(Ni)/Ti AS ELECTROCATALYSTS FOR ALKALINE FUEL CELLS

Loreta Tamašauskaitė-Tamašiūnaitė^{1*}, Aldona Balčiūnaitė^{1,2},
Aušrinė Vaiciukevičienė^{1,3}, Algirdas Selskis¹

- 1 State Research Institute, Center for Physical Sciences and Technology, Institute of Chemistry, A. Goštauto 9, LT-01108, Vilnius, Lithuania
- 2 Vilnius University, Naugarduko 24, LT-03225, Vilnius, Lithuania
- 3 Vilnius Pedagogical University, Studentų 39, LT-08106, Vilnius, Lithuania

ABSTRACT

Platinum-nickel agglomerates were deposited on a titanium surface using a galvanic displacement technique. The electrochemical catalytic activity of this titanium-supported nanoPt(Ni)/Ti electrodes towards the oxidation of borohydride, methanol and ethanol in alkaline media was evaluated by cyclic voltammetry and chronoamperometry. Scanning electron microscopy was used to characterize the surface morphology. The nanoPt(Ni)/Ti catalysts exhibited a higher catalytic efficiency to the oxidation of borohydride, ethanol and methanol as compared with that of the pure Pt.

Key words: PtNi, borohydride oxidation, methanol oxidation, ethanol oxidation, titanium

INTRODUCTION

Direct alcohol fuel cells (DAFCs) are being developed especially for portable power supply. Since borohydride, methanol and ethanol are used as fuel, the development of electrocatalysts having reasonable costs and a high electroactivity for their oxidations is of considerable interest to fuel cells. It is well known that platinum is an effective electrocatalyst for these oxidations [1-6]. Unfortunately, the use of platinum as an electrode material is limited to its scarcity and price. One of ways to reduce the Pt amount is to disperse small Pt particles (in the order of a few nanometers) on a technology relevant substrate. A variety of nanostructured conducting materials like carbon nanotubes, nanofibers and mesoporous carbon were used as supports for Pt catalysts to minimize the use of precious metal. In the present study we investigated the possibility to use the surface of titanium as a support for alkaline fuel cell catalysts. A titanium supported nano-scale bimetallic platinum-nickel catalyst (denoted as nanoPt(Ni)/Ti) was fabricated using a simple procedure known as galvanic displacement [7-13]. This process is based on an electrochemical process, during which the deposition of a noble metal occurs by the oxidation of a precursor

* e-mail: lortam@ktl.mii.lt, tel: (+37)052661291 tel: (+37)052648884

metal adlayer deposited on the substrate at the open-circuit potential. In this study, the spontaneous oxidation of a Ni adlayer by PtCl_6^{2-} ions has been used to produce small Pt particles on the Ti surface. The electrocatalytic activity of the prepared nanoPt(Ni)/Ti catalysts was examined in respect to borohydride, methanol and ethanol oxidation in an alkaline solution by cyclic voltammetry (CV) and chronoamperometry (CA). The surface morphology and composition of the samples were characterized using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDAX).

METHODS OF SAMPLE FABRICATION AND ANALYSIS

Titanium sheets $1 \times 1 \text{ cm}^2$ of 0.127 mm in thickness (99.7% purity, from Aldrich) were degreased with ethanol, rinsed with deionized water and dried in an Ar stream.

Electroless deposition of nickel onto the Ti surface was based on the following procedures: a) activation of the substrate surface in a 0.5 g/l PdCl_2 solution for 1 min; b) rinsing of the treated surface with deionized water and c) immersion into the electroless nickel solution containing 0.1 M NiSO_4 , 0.4 M glycine, 0.25 M sodium hypophosphite and 0.1 M disodium malonate at a constant temperature of 85 °C for 1 min. The solution pH was maintained at 9.0. Platinum particles were deposited on the Ni/Ti electrodes, by immersing them in the solution containing 1 mM H_2PtCl_6 and 0.1 M HCl at room temperature for 15 min. The loading was $1.3 \text{ dm}^2 \text{ g}^{-1}$.

A conventional three-electrode electrochemical cell was used for cyclic voltammetry. The nanoPt(Ni)/Ti and Pt electrodes were employed as the working electrodes, an Ag/AgCl/ KCl_{sat} electrode was used as a reference electrode and a Pt sheet of 2 cm^2 area was used as a counter electrode. A Pt sheet of $1 \times 1 \text{ cm}^2$ geometric area was used as a bulk polycrystalline platinum electrode. The borohydride oxidation was tested in a 1.0 M NaOH solution containing 0.05 M NaBH_4 . The ethanol and methanol oxidations were tested in a 0.5 M NaOH solution containing 2.0 M CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, respectively. The electrolyte solutions were prepared using p.a. grade chemicals and deionized water. All electrochemical measurements were performed with an Eco Chemie Autolab potentiostat (PGSTAT100) using Electrochemical Software (Nova 1.6.013). Steady state linear sweep voltammograms were recorded at a linear potential sweep rate of 50 mV s^{-1} from the stationary E_s value in the anodic direction up to 0.6 V in the alkaline borohydride solution and 0.3 V in the alkaline methanol and ethanol solutions at 25 °C.

The chronoamperometric measurements were carried out by, at first, holding the potential at $E_1 = 0 \text{ V}$ for 10 s, then stepping to potentials -0.8 and 0.3 V for 130 s in the borohydride alkaline solution and to -0.25 V for 130 s in the methanol and ethanol solutions, respectively.

The surface morphology and composition of the samples were character-

ized using a Scanning Electron Microscope EVO-50 EP (Carl Zeiss SMT AG, Germany) with Energy Dispersive and Wave dispersion X-ray Spectrometers (Oxford, UK).

RESULTS AND DISCUSSION

The nanoPt(Ni)/Ti catalysts were fabricated using a simple and low-cost electroless deposition method followed by galvanic displacement of Ni. The electroless nickel film was chosen as an underlayer for the formation of immersion platinum overlayer onto the titanium surface. Due to galvanic displacement platinum deposition, nonspherical platinum crystallites were formed on the Ni surface. The morphology of the nanoPt(Ni)/Ti structure was studied using SEM. The SEM images of the catalyst at different magnifications presented in Figs. 1a, b reveal the presence of nano-scale dendrites with the sizes of ca. 50-100 nm. Light oblong sticks can be resolved in these dendrites.

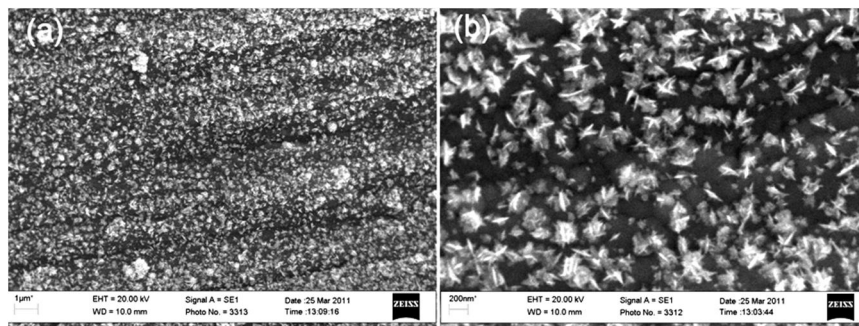


Fig. 1 – SEM micrographs of as-prepared nanoPt(Ni)/Ti under different magnifications

The presence of Pt and Ni onto the titanium surface was confirmed further by Energy dispersive X-ray analysis. According to the data of EDAX analysis, the nanoPt(Ni)/Ti composition was: Pt – 1.49 at.%, Ni – 24.60 at.%, P – 6.81 at.%, O – 25.73 at.% and Ti – 41.37 at.%. The Ni-P layer of about 300 nm was deposited on the titanium surface. It is seen, that a significant remaining of deposited nickel and a much lower amount of Pt on the electrode surface were detected.

Typical cyclic voltammograms of nanoPt(Ni)/Ti (*solid line*) and pure Pt (*dotted line*) electrodes in 0.5 M H₂SO₄ are shown in Fig. 2. The CV profile of the nanoPt(Ni)/Ti shows the usual characteristics of Pt since Ni is electrochemically leached, furthermore, the current for hydrogen adsorption/desorption and oxide formation/reduction on the nanoPt(Ni)/Ti catalyst is much higher than that on Pt. The hydrogen adsorption charge (Q_H) of polycrystalline Pt was calculated at 0.315 mC cm⁻². The nanoPt(Ni)/Ti produced Q_H of 1.41 mC cm⁻². The calculated electroactive surface area (ESA) values are 2.85 and 12.8 cm²

for pure Pt and nanoPt(Ni)/Ti, respectively. The roughness factors are 1.4 and 6.4 for Pt and nanoPt(Ni)/Ti, respectively. These results show that the ESA of the sample is about 4.5 times higher than that of polycrystalline Pt. However, assuming ca. 4.5-fold higher active surface area of Pt(Ni)/Ti compared to smooth polycrystalline Pt, the surface area normalized borohydride oxidation current is ca. 1.5-times higher on Pt. This could be due to ability to oxidize evolved hydrogen at Pt sites, whereas the Pt dendrites are not fully covering the substrate (see Fig. 1b).

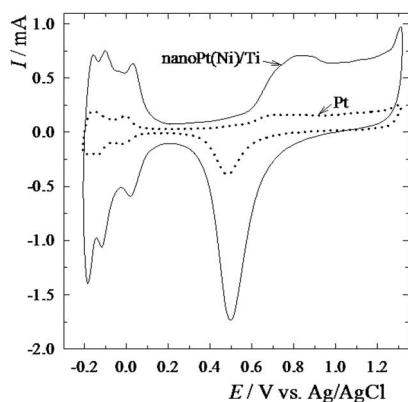


Fig. 2 – CVs of pure Pt (dotted line) and Pt(Ni)/Ti (solid line) in 0.5 M H_2SO_4 at a sweep rate of 50 mV s^{-1}

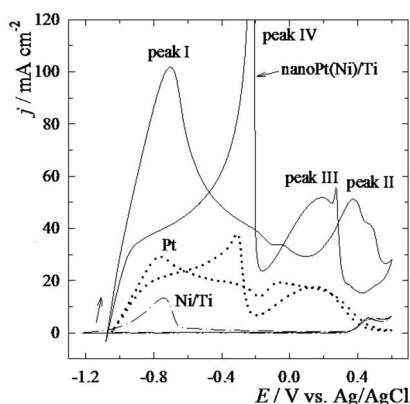


Fig. 3 – CVs of pure Pt (dotted line), nanoPt(Ni)/Ti (solid line) and nanoNi/Ti (dash-dot line) in a 1.0 M NaOH solution containing 0.05 M NaBH_4 at 50 mV s^{-1}

Electrochemical activity of the nanoPt(Ni)/Ti towards borohydride, ethanol and methanol oxidation in an alkaline media was evaluated using cyclic voltammetry and chronoamperometry. Figure 3 presents stabilized cyclic voltammograms (CVs) of pure Pt (dotted line) and nanoPt(Ni)/Ti (solid line) in 1.0 M NaOH containing 0.05 M NaBH_4 at 50 mV s^{-1} . In the forward sweep towards positive potential values the shape of cyclic voltammogram determined in this study for the nanoPt(Ni)/Ti catalyst is similar to the CV onto pure Pt (Fig. 3, compare solid and dotted line), furthermore, the oxidations peaks are significantly higher than that on bare Pt. Anodic peak I seen in CVs for Pt, Ni/Ti and nanoPt(Ni)/Ti catalysts (Fig. 3) is attributed to the oxidation borohydride on Pt generated by catalytic hydrolysis of BH_4^- as described in [14-16] (on nickel borohydride oxidation releases molecular hydrogen). The current density of peak I for the nanostructured electrode is about 3 times higher than that on pure Pt. Peak II which is attributed to direct borohydride oxidation [4, 6] is also about 2-3 times higher as compared to that of pure Pt, but it is shifted

to positive potential values by 0.3 V. Reverse peaks III and IV appear at about the same potential values for nanoPt(Ni)/Ti and Pt, while the nanoPt(Ni)/Ti catalyst produces higher current densities.

The performance of nanoPt(Ni)/Ti catalyst as compared to Pt for both processes: the oxidation of H_2 generated by catalytic hydrolysis of BH_4^- (peak I) and borohydride oxidation (peak II), can be further observed from chronoamperometric measurements. The corresponding curves are shown in Fig. 4. NanoPt(Ni)/Ti and pure Pt catalysts show a current decay for both reactions. At the end of experimental period ($t = 130$ s), the current density of the nanoPt(Ni)/Ti is higher and the current density decay is much slower than that on Pt. NanoPt(Ni)/Ti catalyst has a higher catalytic activity and a better stability for hydrogen and borohydride oxidation, respectively, than Pt. This result is in agreement with the results of cyclic voltammetry curves. Active surface area normalized currents are about 2-3-fold higher at Pt for both oxidations of hydrogen and borohydride than those on nanoPt(Ni)/Ti under chronoamperometric conditions.

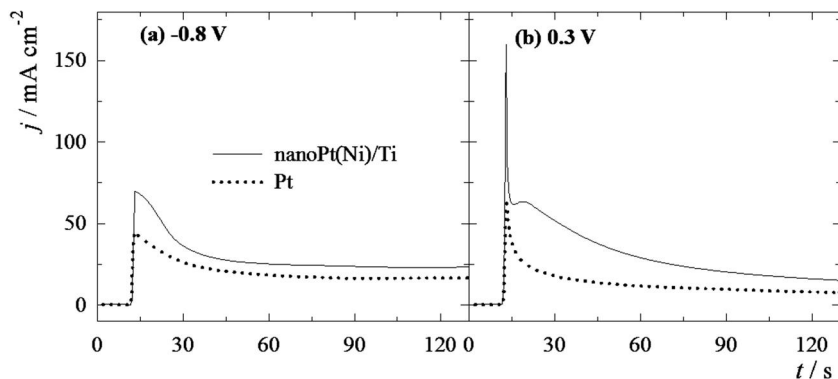


Fig. 4 – Chronoamperometric data from nanoPt(Ni)/Ti (solid lines) and Pt (dotted lines) catalysts studied at -0.8 (a) and 0.3 V (b) in a 1.0 M NaOH containing 0.05 M $NaBH_4$ solution. The potential was firstly held at $E_1 = 0$ V for 10 s, then set to -0.8 and 0.3 V, respectively

Figure 5 presents stabilized cyclic voltammograms after a long-term potential cycling (after 10 cycles) for nanoPt(Ni)/Ti and pure Pt in a 0.5 M NaOH containing 2.0 M C_2H_5OH (a) and 2.0 M CH_3OH (b) at 50 mV s^{-1} . As seen from Fig. 5, the voltammetric curves for oxidation of ethanol (a) and methanol (b) on the nanoPt(Ni)/Ti catalyst are similar in shape with those obtained on the bulk Pt, except for enhanced currents. During the anodic scans, the nanoPt(Ni)/Ti electrocatalyst presents an ethanol and methanol oxidation peaks I at about -0.24 and -0.19 V, respectively (Fig. 5b). About 37 times higher cur-

rent densities for methanol oxidation is obtained on the nanoPt(Ni)/Ti electrode as compared with that on pure Pt. The current density for ethanol oxidation (peak I) is lower as compared to that for methanol oxidation, but higher than that on pure Pt. Active surface area normalized currents are about 1.5-fold lower on the nanoPt(Ni)/Ti catalyst as compared to that on Pt in ethanol solution, therefore, the active surface area normalized currents for methanol oxidation is about 8-fold higher on nanoPt(Ni)/Ti than that on pure Pt.

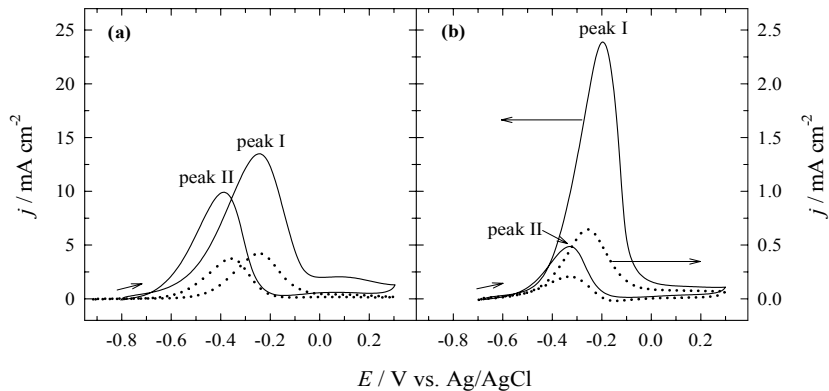


Fig. 5 – CVs of pure Pt (*dotted lines*) and nanoPt(Ni)/Ti (*solid lines*) in a 0.5 M NaOH solution containing 2.0 M C₂H₅OH (a) and 2.0 M CH₃OH (b) at 50 mV s⁻¹

A high electroactivity of nanoPt(Ni)/Ti catalyst compared to Pt was also tested by the chronoamperometry method in alkaline solutions of ethanol (a) and methanol (b). *Figure 6* shows the chronoamperometric data at -0.25 V for the both electrodes.

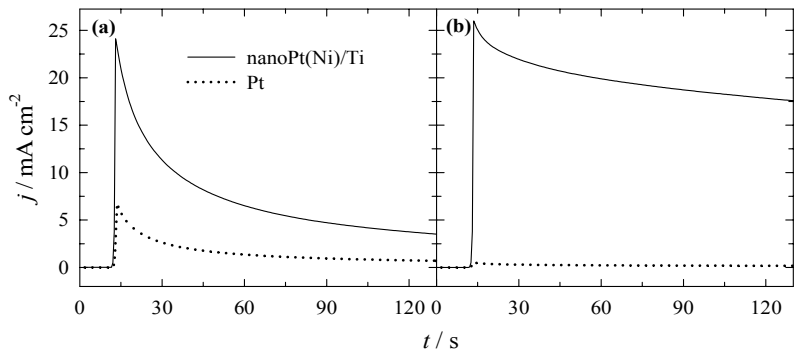


Fig. 6 – Chronoamperometric data from Pt (*dotted lines*) and nanoPt(Ni)/Ti (*solid lines*) catalysts studied at -0.25 V in a 0.5 M NaOH containing 2.0 M C₂H₅OH (a) and 2.0 M CH₃OH (b). The potential was firstly held at *E*₁ = 0 V for 10 s, then set to -0.25 V

The current density for ethanol oxidation on the nanoPt(Ni)/Ti catalyst is much higher and current density decay is much slower as compared to that on bare Pt. A significant increase in steady-state current density for methanol oxidation on the nanoPt(Ni)/Ti catalyst occurs in comparison to pure Pt (Fig. 6b). The steady-state current densities of nanoPt(Ni)/Ti and pure Pt are 17.57 and 0.17 mA cm⁻² ($t = 130$ s), respectively. This shows that the oxidation rate of methanol at -0.25 V on nanoPt(Ni)/Ti is about 100 times higher than that on Pt. Active surface area normalized currents are about of the same value of 0.5 mA cm⁻² for ethanol oxidation on both nanoPt(Ni)/Ti and Pt catalysts, therefore, the active surface area normalized currents for methanol oxidation is about 22-fold higher on nanoPt(Ni)/Ti than that on pure Pt.

The Ni/Ti catalyst with Pt particles 50-100 nm in size shows better performance for oxidation of both ethanol and methanol as compared to that on pure Pt. A higher current density is obtained on this catalyst for methanol oxidation as compared to that for ethanol oxidation.

CONCLUSIONS

In this study we have successfully fabricated an electrode modified with platinum crystallites on the titanium surface, as a substrate, using a simple and low-cost method. For the displacement deposition of Pt crystallites on the titanium surface, the Ni adlayer was used as a precursor. It has been determined that the average size of the Pt crystallites deposited by galvanic displacement of Ni adlayer is about 50-100 nm. The nanoPt(Ni)/Ti catalyst was found to be more active than Pt towards borohydride, methanol and ethanol electro-oxidation in the alkaline media. Also, the nanoPt(Ni)/Ti catalyst shows better voltammetric and chronoamperometric performance for methanol oxidation than for ethanol oxidation.

The fabricated nanoPt(Ni)/Ti catalysts seem to be a promising anodic material for direct alkaline fuel cells. Further investigation is underway.

Acknowledgements

This research was funded by the grant (No. ATE-03/2010) from the Research Council of Lithuania.

REFERENCES

- [1] E. Antolini, J.R.C. Salgado, E.R. Gonzalez, Appl. Catal. B: Environ., 2006, 63, P. 137-149.
- [2] G.A. Camara, T. Iwasita, J. Electroanal. Chem., 2005, 578, P. 315-321.
- [3] M.J. Giz, G.A. Camara, J. Electroanal. Chem, 2009, 625, P. 117-122.
- [4] E.L. Gyenge, Electrochim. Acta, 49, 2004, P. 965-978.
- [5] E.L. Gyenge, M.H. Atwan, D.O. Northwood, J. Electrochem. Soc. 153(1), 2006, P. A150-A158.
- [6] J.I. Martins, M.C. Nunes, J. Power Sources, 175, 2008, P. 244-249.

-
- [7] S.R. Brankovic, J. McBreen, R.R. Adzic, J. Electroanal. Chem., 503, 2001, P. 99-104.
 - [8] K. Sasakia, J.X. Wang, H. Naohara et al. Electrochim. Acta 55, 2010, P. 2645-2652.
 - [9] D. Gokcen, S.-E. Bae, S.R. Brankovic, J. Electrochem. Soc., 157(11), 2010, P. D582-D587.
 - [10] D. Gokcen, S.-E. Bae, S.R. Brankovic, Electrochim. Acta, 56, 2011, P. 5545-5553.
 - [11] S. Papadimitriou, A. Tegou, E. Pavlidou et al., Electrochim. Acta 53, 2008, P. 6559-6567.
 - [12] A. Tegou, S. Aramyanov, E. Valova et al., J. Electroanal. Chem., 634, 2009, P. 104-110.
 - [13] A. Tegou, S. Papadimitriou, I. Mintsouli et al. Catal.Today, 170, 2011, P. 126-133.
 - [14] B.H. Liu, Z.P. Li, S. Suda, J. Electrochem. Soc. 150(3), 2003, P. A398-A402.
 - [15] K.M. Gorbunova, M.V. Ivanov, V.P. Moiseev, J. Electrochem. Soc., 120, 1973, P. 613-618.
 - [16] J.S. Walter, A. Zurawski, D. Montgomery et al. J. Power Sources, 179, 2008, P. 335-339.